

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Etching Process

We, NORTH AMERICAN ALUMINUM CORPORATION, a corporation organized and existing under the laws of the State of Michigan, of 5575 North Riverview Drive, Parchment, Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for etching aluminum alloys and, more particularly, relates to a process, as aforesaid, in which the etched products have a substantially uniform gloss finish from piece to piece and in which the etchant bath has a much longer useful life than it has heretofore been possible to achieve.

It is well known to etch aluminum alloy articles by immersing such articles in hot aqueous alkali solutions, for example, a sodium hydroxide solution. The etched article is then treated with a suitable acid to remove "smut", following which the etched article can be rinsed and dried or processed further such as in anodizing.

The following description with respect to aluminum alloy extrusions has reference to alloys of the following range of compositions:

Si	.2—8%
Fe	.4% (max.)
Cu	.2% (max.)
Mg	.3—1.0%

All other elements, except aluminium, .1% max. for each element

Al

Balance

The following discussion with respect to aluminium alloy sheets shall have reference to alloys of the following range of compositions:

Si+Fe	.45% (max.)
Cu	.1% (max.)
Mg	2.2—2.8%
Cr	.15—.25

All other elements, except aluminium, .1% max. for each element.

Al

Balance

A prime factor limiting the useful life of the etchant bath for etching aluminium extrusions of the composition aforesaid for decorative or architectural purposes is that sooner or later "galvanizing" of the surfaces of the etched products will occur. "Galvanizing" as used herein refers to the phenomena according to which the grain located near the surface of the aluminium extrusion becomes relatively highly visible.

It may be noted here that the galvanizing problem appears to be limited to aluminium extrusions because aluminium alloy sheets, for example, as a result of their smaller grain size and other metallurgical factors, do not appear to be subject to galvanizing. Moreover, aluminium alloy castings, although having a larger grain size are subject to having nonuniform composition and porosity and therefore have only limited use for decorative or architectural purposes. The previous theory has been that galvanizing is the result of aluminium build-up in the etchant bath. It has been considered that the maximum aluminium concentration in the etchant bath that can be tolerated, and still entirely avoid "galvanizing", is approximately 25 g. of dissolved aluminium per litre.

While it has long been desirable that aluminium alloy extrusions and sheets of the compositions mentioned above, intended for architectural purposes, have a surface finish of uniform gloss, it has been difficult heretofore to achieve such a finish which is uniform from piece to piece. This is largely due

- extruded  
- etched  
- anodized  
- no aging

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to the fact that as the amount of dissolved aluminium in the bath increases, the activity of the bath changes. In working with this problem, we have discovered that etched finishes of substantially uniform gloss can be obtained on aluminium alloy extrusions and sheets, of the compositions mentioned above, provided that the etchant bath contains at least about 50 gms. of dissolved aluminium per litre and further that such etched finishes will remain substantially uniform from piece to piece so long as the dissolved aluminium concentration in the bath is substantially constant during an extended production run. Uniform gloss is achieved using production baths having a substantially constant dissolved aluminium concentration so long as same is within the range of 50 to 100 or more gms. per litre.

The gloss of aluminium extrusions can be measured by a suitable gloss meter. Such meters are graduated to indicate the gloss of the surface measured. Readings can be based on a perfect mirror finish having a reading of 1000. The aluminium alloy extrusions and sheets produced by the invention under typical conditions have a gloss measured at 45° to the surface of about 170 when the dissolved aluminium concentration in the bath is 50 grams per litre and they have a gloss of about 200 when the dissolved aluminum concentration is about 80 grams per litre. For high quality, uniform gloss work, the gloss reading should be maintained within a range of not more than about  $\pm 20\%$  of the median gloss reading.

In carrying out the etching process using an etchant bath containing at least 30 grams of dissolved aluminium per litre, the "galvanizing" problem on aluminium extrusions referred to above has been encountered and this has necessitated frequent changes of the etchant bath. This represents a substantial cost item not only because of the cost of the etchant material itself but also because of the time and the labour cost involved in changing the bath.

While it would appear, from the prior knowledge, that the problems of eliminating "galvanizing" and at the same time achieving a uniform gloss finish on aluminium alloy extrusions of the composition referred to above using a long-lived etchant bath involved mutually inconsistent solutions, we have discovered that these problems can be solved simultaneously if there is added to the etchant bath a suitable material for insuring the presence of sulphide ions therein. We have discovered that the cause of the "galvanizing" problem in etchant baths having a high dissolved aluminium concentration is the dissolved zinc which also becomes present in the etchant bath. As little as four or five parts per million of zinc in the etchant bath containing a high dissolved aluminium concentration is capable of causing galvanizing. The

aluminium alloy that is being etched is the major source of the dissolved zinc, although other possible sources include the make-up water supplied, and impurities in the proprietary etchant. A typical value for zinc which is present in 6063 aluminum alloy is .02%. It has been found that the presence of small amount of sulphide ions in the etchant bath will precipitate the zinc sulphide and that such substantially eliminates the problem of galvanizing in etchant baths having a high dissolved aluminium concentration.

According to the invention, there is provided a method of etching an aluminium alloy product which comprises treating the product with an alkali etching solution having dissolved therein at least about 50 g. of aluminium per litre and also having present therein a positive concentration of sulphide ions. For uniform gloss products of either the extrusion or sheet type having the compositions referred to above, the minimum dissolved aluminium concentration is 50 grams per litre. The etched surface of an extrusion thus treated is free of galvanizing effects caused by the etch bath and is smooth and has a uniform gloss as the bath ages further. This gloss will be substantially uniform for all aluminium alloy extrusions and sheets treated by the same type of bath under similar conditions of time, temperature and alkali concentration in the bath. Moreover, the useful life of the bath will be of indefinite duration, provided that suitable amounts of make-up chemicals are added thereto from time to time to maintain the desired concentrations of such chemicals.

The method according to the invention can be carried out on aluminium sheets or extrusions of the compositions referred to above, it being noted here that the invention does not pertain to the treatment of other aluminium alloys. An aluminium alloy which provides especially good results is the commercially available alloy 6063. However, other 6063 type aluminium alloys can be etched according to the invention to obtain similar results.

The etching treatment is carried out in a hot aqueous alkali solution containing, for example, sodium or potassium hydroxide, or other alkaline materials, sodium hydroxide, being preferred. The alkali concentration of the etchant bath is not critical and such concentration can range from 2 oz. alkali/gallon of water to 10 oz. alkali/gallon of water. The alkali solution also can contain various conventional noncritical additives, such as sodium gluconate, which are added to improve the etching effect, prevent scale formation, and the like.

The alkali solution must contain at least about 50 grams of dissolved aluminium per litre in order to achieve the desired uniform gloss on the surface of the treated aluminium

alloy products. Lesser amount of dissolved aluminium in the etchant bath will cause variations in the gloss of the etched extrusion which are difficult to control. The maximum dissolved aluminium concentration in the etching bath is limited only by the ability of the etchant solution to retain the aluminium in solution. This is affected by a variety of factors, including particularly the temperature of the solution. It has been found that when a suitable temperature is maintained, the concentration of the dissolved aluminium in the etchant bath can be as high as about 90—105 grams per litre without difficulty, and even higher dissolved aluminium concentrations can be used in appropriate cases.

As indicated above, there will be some variation in the gloss level depending on the concentration of the dissolved aluminium in the etchant bath. During start up with a fresh etchant bath, it will be advisable to build up the concentration of the dissolved aluminium to the desired level before etching the parts which require a uniform gloss. This can be done by etching scrap aluminium pieces, by using the bath to etch pieces which do not require a uniform gloss, or by employing part of an existing bath as make up for the new bath.

While aluminium is continuously being dissolved in the etchant bath as the extrusions are etched so that the aluminium concentration of the bath tends to rise, this presents no serious problem because some of the dissolved aluminium is continually being removed from the etchant bath with the etched products. That is, a certain amount of the etchant bath will adhere to the etched extrusion or will collect in pockets therein and the same will be removed from the remainder of the bath along with the extrusion. This removal of a part of the etchant is commonly termed "drag out". It is customary to add fresh etching solution to the bath from time to time in order to make up for the part that is removed from the bath with the etched product and to make up for that consumed in one chemical reaction. Since the make-up etching solution is free of aluminium, the aluminium concentration in the etchant bath is thereby maintained within fairly constant limits because the rate at which the aluminium is dissolved from the etched products becomes more or less equal to the amount of dissolved aluminium that is removed from the bath as a result of the "drag out".

The temperature of the etchant bath may vary from 100° F. to 180° F. It has been found satisfactory to use etching times of from 1 to 30 minutes.

A positive sulphide ion concentration is maintained in the etchant bath at all times in order to precipitate zinc as zinc sulphide. Because of the low solubility of zinc sulphide

in alkaline aqueous solutions, it is possible to maintain the residual zinc concentration in the bath at a sufficiently low level that galvanizing does not occur. The sulphide ion concentration is continuously maintained at a level of from four to eight gms. per litre (calculated as sodium sulphide) in order to assure precipitation of the zinc. A higher level of the sulphide concentration can be maintained, if desired, but such is not necessary. Similarly, lower concentrations of the sulphide ions can be used, provided that at all times there is a positive sulphide concentration in the etchant bath, but lower amounts increase the risk that galvanizing will occur. Desirably the sulphide material is added to the bath from time to time to make up for the part thereof which precipitates with the zinc and other alkali insoluble metallic sulphides and also, the part that leaves the bath with the etched product as a result of the "drag out". The sulphide material will be required at a rate of one to ten gms. for each 100 gms. of the make-up etchant material added to the bath. Examples of the sulphide ions supplying material that can be used include hydrogen sulphide, alkali sulphides and polysulphides, sodium sulphide being preferred. These materials may be employed individually or as a mixture of two or more of these materials.

It will be understood that the so-called "smut" remaining on the surface of the extrusion after etching can be removed in any suitable convenient fashion. As this procedure is conventional and well known and forms no part of the invention, a detailed description thereof is believed unnecessary.

Gloss differences can be minimized by anodizing or other after treatment.

#### EXAMPLES

I. An extrusion of 6063 alloy was etched for 10 minutes at 130° F. in an aqueous solution containing 5 oz. per gallon of NaOH, 2 gms. per litre sorbitol, 50 gms. per litre dissolved aluminium, and 4 gms. per litre dissolved  $\text{Na}_2\text{S}$ . The extrusion was then rinsed in tap water and "desmutted" in 30% by weight  $\text{HNO}_3$  acid. No galvanizing occurred and the gloss measurement was 170 as measured in the same manner as sample I.

II. Repeat of I using 70 gms. per litre aluminium. Gloss 200:

III. Repeat of I using 90 gms. per litre aluminium. Gloss 220.

#### WHAT WE CLAIM IS:—

1. A process of etching (a) aluminium alloy extrusions having the following composition Si=.2—.8%, Fe=.4% (max), Cu=.2% (max), Mg=.3—1.0%; all other elements except aluminium being less than .1% each and the balance being aluminium, and (b)

- aluminium alloy sheets having the following composition Si+Fe=.45% (max), Cu=.1% (max), Mg=2.2—2.8%, Cr=.15—.25%, all other elements except aluminium being less than .1% each and the balance being aluminium, to produce a uniform gloss finish thereon, which comprises: treating said aluminium alloy pieces with an alkali etching solution having dissolved therein at least about 50 gms. per litre of aluminium and having present therein sulphide ions in order to precipitate zinc which may be present in the etching solution.
2. A process according to Claim 1, in which the maximum aluminium concentration in the etching solution is about 105 gms. per litre.
3. A process according to Claim 1, in which the sulphide ions are obtained by dissolving in the etching solution materials selected from the group consisting of sulphides and polysulphides of alkali metals.
4. A process according to Claim 1, in which the sulphide ions are obtained by dissolving sodium sulphide in the etching solution.
5. A process according to Claim 1, in which the temperature of the etching solution is maintained between 100° F. and 180° F. and the aluminum alloy pieces are immersed in the etching solution for from 1 to 30 minutes.
6. A process of etching, substantially as hereinbefore described.
7. The product of the process of any of the preceding claims.

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